

### Hydroxysulfate surface treatment

The present invention relates to the use of a treatment solution for treating the surface of a steel sheet coated with a metal coating based on zinc or its alloys. It also relates to a method of lubricating such a coated sheet.

Steel sheet coated with zinc or its alloys is widely used in the automotive field and in industry in general, as it exhibits excellent corrosion resistance. However, such galvanized steel sheet has a number of difficulties when it is being formed, for example by drawing, in order to manufacture parts.

Usually, to give galvanized steel sheet better tribological properties, a film of lubricating oil is applied to its surface so as to facilitate the forming operation.

However, despite applying a suitable lubricating oil film, very substantial friction exerted by forming tools on the surface of the sheet causes, at the surface of the sheet, powder or particles based on zinc or its alloys that are generated by degradation of the coating. The accumulation and/or agglomeration of these particles or this powder in the forming tools may damage the formed parts, by the formation of barbs and/or constrictions.

Furthermore, because of the high friction coefficient that characterizes the sliding of a galvanized surface in contact with the surface of a forming tool, the sheet runs the risk of fracturing should there be insufficient sliding of the sheet in the forming tool gap. Such fractures may appear even when an oil film of sufficient weight, i.e. greater than  $1 \text{ g/m}^2$ , is applied to the surface of the sheet as it is not possible to maintain a uniform distribution of the oil film over

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the surface of the sheet. This is due to the phenomenon of dewetting, which corresponds to the presence of areas deficient in oil.

5 However, the fact of depositing a relatively thick oil film on the surface of the sheet poses problems of contamination of the workshops and drawing tools, and requires the use of large quantities of degreasing agents in order to clean the sheet and considerable  
10 means for treating the effluents coming from the cleaning operation.

Moreover, the oil deficiency in certain areas of the oil film due to the dewetting effect is also  
15 responsible for lesser temporary corrosion protection of the steel sheet while it is being stored.

The object of the present invention is therefore to propose a treatment solution which, when applied to the  
20 surface of a steel sheet coated with a metal layer based on zinc or its alloys, makes it possible to reduce the degradation of the galvanized surface of this sheet while it is being formed, to reduce the quantity of lubricating oil to be deposited on the  
25 sheet before it is formed, and to improve the temporary corrosion protection of the sheet.

For this purpose, the subject of the invention is the use of an aqueous treatment solution containing sulfate  
30 ions  $\text{SO}_4^{2-}$  with a concentration of not less than 0.01 mol/l in order to treat the surface of a steel sheet treated on at least one of its sides with a metal coating based on zinc or its alloys, for the purpose of reducing the formation of metal powder or particles  
35 based on zinc or its alloys generated by the degradation of the coating while said sheet is being formed.

The expression "metal coating based on a zinc alloy" is

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understood to mean a zinc coating comprising one or more alloying elements, such as for example but not being restricted thereto, iron, aluminum, silicon, magnesium and nickel.

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According to the invention, the use of a steel sheet coated with an almost pure zinc coating is preferred.

10 When the surface of a steel sheet coated with a metal coating based on zinc or its alloys is treated by means of an aqueous treatment solution according to the invention, a layer forms on the surface of the sheet that is based on zinc hydroxysulfate and zinc sulfate and is both sufficiently thick and sufficiently  
15 adherent. However, such a layer cannot be formed when the  $\text{SO}_4^{2-}$  concentration is less than 0.01 mol/l, but it has also been found that too high a concentration does not substantially improve the rate of deposition and may even slightly reduce it.

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In a first embodiment of the invention, the treatment solution is applied in a conventional manner, for example by dipping, by spraying or by coating, both on electrogalvanized sheet and on hot-dip galvanized  
25 sheet.

In a preferred embodiment, the aqueous treatment solution furthermore contains  $\text{Zn}^{2+}$  ions with a concentration of not less than 0.01 mol/l which makes  
30 it possible to obtain a more uniform deposition.

For example, the treatment solution is prepared by dissolving zinc sulfate in pure water; for example, zinc sulfate heptahydrate ( $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ ) is used, the  $\text{Zn}^{2+}$   
35 ion concentration then being equal to that of the  $\text{SO}_4^{2-}$  anions.

Preferably, the pH of the treatment solution corresponds to the natural pH of the solution without

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the addition of either base or acid - the value of this pH is generally between 5 and 7.

To minimize the formation of powder or particles of zinc or its alloys resulting from degradation of the coating on the sheet while it is being formed, the conditions under which the treatment solution is applied to the surface of the sheet, namely the temperature, the time during which the solution is in contact with the galvanized surface, the  $\text{SO}_4^{2-}$  ion concentration and the  $\text{Zn}^{2+}$  ion concentration, are adjusted so as to form a layer based on zinc hydroxysulfate and zinc sulfate, the sulfur content of which is not less than  $0.5 \text{ mg/m}^2$ . This is because when the sulfur content is less than  $0.5 \text{ mg/m}^2$ , the reduction in degradation of the coating is less substantial.

Thus, the time during which the treatment solution is in contact with the galvanized surface is between two seconds and two minutes and the temperature of the treatment solution is between  $20$  and  $60^\circ\text{C}$ .

Preferably, the treatment solution used contains between  $20$  and  $160 \text{ g/l}$  of zinc sulfate heptahydrate, which corresponds to a  $\text{Zn}^{2+}$  ion concentration and an  $\text{SO}_4^{2-}$  ion concentration that lie between  $0.07$  and  $0.55 \text{ mol/l}$ . In fact, it has been found that in this concentration range the rate of deposition is barely influenced by the value of the concentration.

Advantageously, the conditions under which the treatment solution is applied, namely the temperature, the time during which the solution is in contact with the galvanized surface and the  $\text{SO}_4^{2-}$  ion and  $\text{Zn}^{2+}$  ion concentrations, are adjusted so as to form a hydroxy-sulfate/sulfate-based layer having a sulfur content of between  $3.7$  and  $27 \text{ mg/m}^2$ .

According to a variant of the invention, the treatment

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solution contains an oxidizing agent for zinc, such as hydrogen peroxide. This oxidizing agent may have a very pronounced sulfation/hydroxysulfation accelerator effect at low concentration. It has been found that the  
5 addition of only 0.03%, i.e.  $8 \times 10^{-3}$  mol/l of hydrogen peroxide, or of  $2 \times 10^{-4}$  mol/l of potassium permanganate, to the solution makes it possible for the rate of deposition to be doubled (approximately). However, it has been found that concentrations 100  
10 times higher no longer allow this improvement in deposition rate to be obtained.

After the treatment solution has been applied, but before drying, the layer deposited on the sheet is  
15 adherent. The drying is adjusted in order to remove the residual liquid water from the deposit.

Between the application step and the drying step, the sheet is preferably rinsed so as to remove the soluble  
20 portion of the deposit obtained. The absence of rinsing and the formation of a resulting deposit that is partially soluble in water do not greatly prejudice the reduction in degradation of the galvanized coating during the operation of forming the sheet, since the  
25 deposit obtained does indeed comprise a water-insoluble zinc hydroxysulfate/zinc sulfate-based layer in contact with the sheet.

According to a second embodiment of the invention, the  
30 aqueous treatment solution having an  $\text{SO}_4^{2-}$  ion concentration of not less than 0.01 mol/l is applied under anodic polarization and the pH of the treatment solution is equal to 12 or higher, but less than 13.

35 If the pH of the solution is less than 12, adherent hydroxysulfates are not formed on the surface to be treated. If the pH of the solution is equal to 13 or higher, the hydroxysulfate redissolves and/or decomposes into zinc hydroxides.

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When sodium sulfate is used in the treatment solution, if the sodium sulfate concentration is less than 1.4 g/l in the solution, little formation of hydroxysulfates on the surface is observed. More generally, it is therefore important for the  $\text{SO}_4^{2-}$  ion concentration to be not less than 0.01 mol/l, and preferably not less than 0.07 mol/l.

Furthermore, the sulfate ion concentration is preferably not more than 1 mol/l. If sodium sulfate is used, at concentrations greater than 142 g/l (equivalent to 1 mol/l of  $\text{SO}_4^{2-}$ ), for example 180 g/l, a reduction in the efficiency of formation of the zinc hydroxysulfate/zinc sulfate-based layer is observed.

It has been found that the reduction in degradation of the galvanized coating of the sheet while it is being formed is obtained only if the thickness of the zinc hydroxysulfate/zinc sulfate-based layer deposited corresponds to more than 0.5 mg/m<sup>2</sup> of equivalent sulfur, preferably at least 3.5 mg/m<sup>2</sup> of equivalent sulfur.

However, it has been found that the reduction in degradation of the galvanized coating decreases if the amount of sulfur in the zinc hydroxysulfate/zinc sulfate-based layer deposited greatly exceeds 30 mg/m<sup>2</sup>, owing, it would seem, to the deterioration in adhesion of this layer.

Thus, to reduce the deterioration of the galvanized coating, significantly, it is necessary for the total deposited amount of hydroxysulfates and sulfates to be not less than 0.5 mg/m<sup>2</sup> but not to exceed 30 mg/m<sup>2</sup> of equivalent sulfur, preferably to be between 3.5 and 27 mg/m<sup>2</sup> of equivalent sulfur.

The zinc needed to form the zinc hydroxysulfate/zinc sulfate-based deposit comes from the anodic dissolution

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of zinc under the effect of the polarization of the galvanized surface.

It is therefore necessary for the density of electrical  
5 charges flowing during the treatment through the surface of the sheet to be adjusted so as to form a zinc hydroxysulfate/zinc sulfate-based layer having a sulfur content of not less than 0.5 mg/m<sup>2</sup>.

10 Thus, the applied charge density is preferably between 10 and 100 C/dm<sup>2</sup> of surface to be treated.

If the charge density exceeds 100 C/dm<sup>2</sup>, it has been  
found that the amount of sulfur deposited on the  
15 surface no longer increases, and even decreases.

Thanks to the anodic polarization of the galvanized surface to be treated, there is rapid dissolution of the zinc in the immediate vicinity of the galvanized  
20 surface, which promotes the precipitation of zinc salts on this surface.

Thus, to carry out this treatment in as productive a manner as possible with a satisfactory coulombic  
25 efficiency, it is necessary for the zinc hydroxysulfate/zinc sulfate-based layer to be deposited under a high polarization current density, especially greater than 20 A/dm<sup>2</sup>, for example 200 A/dm<sup>2</sup>.

30 At a current density of less than or equal to 20 A/dm<sup>2</sup>, the deposition efficiency is very low and the amount of sulfur in the deposited layer does not make it possible to significantly reduce the degradation of the zinc coating on the sheet while it is being formed.

35 As counter-electrode, it is possible to use a titanium cathode.

The temperature of the treatment solution is generally

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between 20°C and 60°C. Preferably, the treatment is carried out at a temperature of 40°C or higher, so as to increase the conductivity of the solution and to reduce the ohmic losses.

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The flow rate of the solution at the surface of the sheet does not, here, have any major impact on the treatment according to the invention.

- 10 After the hydroxysulfate/sulfate-based layer has been formed on the surface, the coated surface is thoroughly rinsed with demineralized water. This rinsing step is important in order to remove the alkaline reactants at the surface of the deposit, reactants that might cause  
15 corrosion problems.

The subject of the invention is also a method of lubricating a steel sheet coated with a layer consisting of a metal coating based on zinc or its  
20 alloys, in which method:

- said sheet is coated with an upper layer based on zinc hydroxysulfate and zinc sulfate, said upper layer having been obtained by using a treatment solution according to the invention; and then
- 25 - a lubricating oil film is applied to the upper layer with a weight of less than 1 g/m<sup>2</sup>.

The weight of lubricating oil film applied is preferably less than 0.9 g/m<sup>2</sup> and is more particularly  
30 between 0.2 and 0.5 g/m<sup>2</sup>, since such weights are sufficient to obtain excellent temporary corrosion protection and to avoid any risk of contamination of workshops and forming tools.

- 35 Finally, the subject of the invention is the use of an aqueous treatment solution comprising sulfate ions with a concentration of not less than 0.01 mol/l, in order to improve temporary corrosion protection of a steel sheet coated with a metal layer based on zinc or its



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alloys.

This aqueous treatment solution is applied to the steel sheet according to the embodiments described in the paragraphs relating to the use of an aqueous treatment solution containing sulfate ions for treating a galvanized steel sheet for the purpose of reducing degradation of the zinc coating while the sheet is being formed. For this purpose, the reader may refer to the paragraphs relating thereto.

As will be seen in the examples illustrating the invention, the inventors have shown that the temporary corrosion protection of a galvanized steel sheet firstly treated with a treatment solution according to the invention and then coated with an oil film is very much better than that of a galvanized steel sheet that has not been treated beforehand.

The invention will now be described by examples given by way of nonlimiting indication and with reference to the appended figures in which:

- Figure 1, with reference to Example 2, illustrates the results of the friction tests carried out on various sheet test pieces treated according to the invention or untreated; and

- Figure 2, with reference to Example 3, illustrates the results of the hot/wet corrosion tests carried out on various sheet test pieces according to the invention or untreated.

**1. Reduction in the formation of coating powder or particles when drawing a galvanized sheet**

Test pieces were cut from a steel sheet, of "aluminum-killed steel" grade and of ES quality, with a thickness of 0.7 mm and coated on each of its sides with a zinc coating produced by hot dipping in a zinc bath.

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An aqueous treatment solution according to the invention, obtained from 125 g/l of zinc sulfate heptahydrate  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  was prepared.

5 Next, this treatment solution was applied to some of the test pieces by spraying the treatment solution at a temperature of 40°C. After the sheet was in contact with the solution for a time of 3 to 4 s, the treated sheet was drained and then dried.

10

A lubricating oil film was then applied to the zinc hydroxysulfate/zinc sulfate-based layer formed on the surface of the galvanized steel sheet test pieces, said oil being either QUAKER 6130 oil (from Quaker) or  
15 FUCHS 4107S oil (from Fuchs), with a film weight of 1.5 g/m<sup>2</sup>.

The other test pieces that had not been pretreated with the treatment solution according to the invention were  
20 oiled, either with the QUAKER 6130 oil or with the FUCHS 4107S oil, again with a film weight of 1.5 g/m<sup>2</sup>.

The two series of test pieces were then subjected to a controlled deformation test by means of a press  
25 comprising a punch, a die and a blank holder, recreating in the laboratory the stresses undergone by the sheet during a drawing operation, especially in the die radii and/or in the retaining rings with which the drawing tools are equipped. Various blank-holder  
30 clamping forces were applied to the test pieces undergoing the test.

Each of the test pieces of the two series was weighed before the oiling operation and then at the end of the  
35 test, after de-oiling, by means of a balance accurate to 0.0001 grams. The measured difference in weight was normalized to a weight loss per square meter, taking into account the area affected by the friction during the simulation of drawing the test piece, which was

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identical for each of the test pieces.

Moreover, after having formed one test piece and before the next test piece was formed, the press was wiped so as to identify the zinc coating powder or particles lost by the test piece in the press.

The weight loss results of the test pieces after drawing and the identification of zinc powder and/or particles coming from the coating are given in Table 1. The particles and/or powder are identified by a rating in the following manner, according to a scale ranging from 1 to 4, where:

rating 1: very few particles or very little powder;

rating 2: few particles or little powder;

rating 3: many particles or a lot of powder; and

rating 4: very high level of particles or powder.

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Table 1: Test results

	Type of oil (quantity: 1.5 g/m <sup>2</sup> per side)	Clamping force (daN)	Weight loss (g/m <sup>2</sup> )	Identification on the tools	
				Powder	Particles
Steel sheet coated with lubricating oil film	QUAKER oil	400	0.63 ± 0.04	3	3
	FUCHS oil	400	0.55 ± 0.04	3	3
Steel sheet coated with a hydroxy- sulfate layer and with a lubricating oil film	QUAKER oil	400	0.12 ± 0.1	2	1
		750	0.22 ± 0.1	3	1 to 2
	FUCHS oil	750	0.20 ± 0.1	3	1

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The measured weight losses and the amounts of powder and particles observed when wiping the tools show that the loss of material from the zinc coating, due to the galvanized steel sheet passing over the punch, is significantly reduced when the sheet, before being oiled, is treated with the treatment solution according to the invention.

10 **2. Reduction in the effect of dewetting - effect on the tribological behavior - friction test**

Test pieces 1 cm<sup>2</sup> in area were cut from a steel sheet, of "aluminum-killed steel" grade and of ES quality, with a thickness of 0.7 mm and coated on each of its sides with a zinc coating produced by hot dipping in a zinc bath.

Some of these test pieces were treated with a treatment solution according to the invention, under the same conditions as those indicated in Example 1, so as to form a zinc hydroxysulfate/zinc sulfate-based layer. A lubricating oil film (QUAKER 6130 oil) is then applied to this layer in amounts ranging between 0.25 and 2.5 g/m<sup>2</sup>.

25 The other test pieces were oiled in the same manner as previously, but without having been pretreated with the treatment solution according to the invention.

30 The friction behavior of each of the test pieces was then characterized using a tribology tester in the following manner.

The tester was a flat-on-flat tribometer known per se. 35 The test pieces to be tested were clamped with a clamping force  $F_c$  between two high-speed steel plates offering a bearing (or sliding) surface to the test pieces. The friction coefficient  $N$  was measured while moving the test piece relative to the plates over a

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total travel  $D$  of 180 mm and at a speed of 10 mm/s, while progressively increasing the clamping force  $F_c$ .

5 A curve showing the variation in friction coefficient as a function of the clamping force  $F_c$  for different lubricating oil film weights can then be plotted (see Figure 1).

10 The various curves are identified by the following symbols:

+: sheet treated according to the invention and then coated with  $0.25 \text{ g/m}^2$  per side of a QUAKER 6130 oil film;

15 x: sheet treated according to the invention and then coated with  $1.0 \text{ g/m}^2$  per side of a QUAKER 6130 oil;

•: sheet treated according to the invention and then coated with  $2.5 \text{ g/m}^2$  per side of a QUAKER 6130 oil film;

20 ■: untreated sheet coated with  $0.25 \text{ g/m}^2$  per side of a QUAKER 6130 oil film;

▲: untreated sheet coated with  $1.0 \text{ g/m}^2$  per side of a QUAKER 6130 oil film; and

♦: untreated sheet coated with  $2.5 \text{ g/m}^2$  per side of a QUAKER 6130 oil film.

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Given in Table 2, for each of the test pieces tested, is the mean value of the friction coefficient for a given clamping force  $F_c$ .

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Table 2

Clamping force (MPa)	Friction coefficient					
	Weight of oil on the sheet treated according to the invention			Weight of oil on the untreated sheet		
	0.25 (g/m <sup>2</sup> )	1.0 (g/m <sup>2</sup> )	2.5 (g/m <sup>2</sup> )	0.25 (g/m <sup>2</sup> )	1.0 (g/m <sup>2</sup> )	2.5 (g/m <sup>2</sup> )
30	0.13	0.12	0.12	0.20	0.15	0.15
50	0.11	0.11	0.11	0.20	0.17	0.17

5 The results obtained show that a reduction in the weight of oil results in a substantial increase in the friction coefficient when no treatment solution according to the invention is applied before applying the oil film.

10

However, when the treatment solution according to the invention has been applied to the galvanized sheet prior to application of the lubricating oil film, the friction coefficients obtained are very low, even with  
15 oil weights of less than 0.5 g/m<sup>2</sup>.

### **3. Reduction in the effect of the dewetting - the effect on temporary corrosion protection**

20 Test pieces were cut from a steel sheet, of "aluminum-killed steel" grade and of ES quality, with a thickness of 0.7 mm and coated on each of its sides with a zinc coating produced by hot dipping in a zinc bath.

25 Some of these test pieces were treated with a treatment solution according to the invention, under the same conditions as those indicated in Example 1, so as to form a zinc hydroxysulfate/zinc sulfate-based layer. A lubricating oil film (QUAKER 6130 oil) was then applied

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to this layer in weights ranging between 0.25 and 1.0 g/m<sup>2</sup>.

5 The other test pieces were oiled in the same manner as previously, but without having been pretreated with the treatment solution according to the invention.

10 The lubricating oils applied to the steel sheets coated with the zinc-based metal coating guaranteed corrosion protection during the period of time that elapsed between manufacture of the sheets and their processing, for example by drawing.

15 The conformity of the product delivered up to this point was checked via the results of an accelerated hot/wet corrosion test.

20 Specifically, the test pieces to be tested were placed in an environmental chamber corresponding to the DIN 50017 standard, which simulates the conditions for corrosion of the external turn of a coil of sheet or of an individual cut sheet during storage.

25 The details of the hot/wet cycle (one cycle = 24 hours) are given below:

- 8 h at 40°C and 95-100% RH (relative humidity);
- 16 h at 20°C and 75% RH.

30 The individual test pieces were suspended vertically.

The results of the test, given in Table 3, were obtained by measuring the number of successive cycles before any traces of corrosion appeared on the test piece.

35 A curve showing the variation in the percentage content of white rust as a function of the number of cycles for each of the test pieces tested can then be plotted (cf. Figure 2).

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The various curves are identified by the following symbols:

5       +: sheet treated according to the invention and then coated with 0.25 g/m<sup>2</sup> per side of a QUAKER 6130 oil film;

         \*: sheet treated according to the invention and then coated with 0.5 g/m<sup>2</sup> per side of a QUAKER 6130 oil film;

10       ▲: sheet treated according to the invention and then coated with 1.0 g/m<sup>2</sup> per side of a QUAKER 6130 oil film;

         ♦: untreated sheet coated with 0.25 g/m<sup>2</sup> per side of a QUAKER 6130 oil film;

15       ■: untreated sheet coated with 0.5 g/m<sup>2</sup> per side of a QUAKER 6130 oil film; and

         •: untreated sheet coated with 1.0 g/m<sup>2</sup> per side of a QUAKER 6130 oil film.

20

Table 3

Number of cycles	% rust					
	Weight of oil on the sheet treated according to the invention			Weight of oil on the untreated sheet		
	0.25 (g/m <sup>2</sup> )	0.5 (g/m <sup>2</sup> )	1.0 (g/m <sup>2</sup> )	0.25 (g/m <sup>2</sup> )	0.5 (g/m <sup>2</sup> )	1.0 (g/m <sup>2</sup> )
0.5	5%	0%	0%	60%	20%	0%
1.5			0%	85%		2%
2.5		2%	0%			2%
3.5	20%	2%	0%			2%
4.5	30%		0%		40%	2%
5.5	55%		0%		50%	2%
8.5		12%	0%		65%	2%

It has been found that it is possible to very significantly improve the temporary corrosion



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protection of galvanized steel sheets to which a treatment solution according to the invention has been applied before application of the lubricating oil film, this being so even when the weight of oil is less than  
5 1 g/m<sup>2</sup>.